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ANALYSIS OF LIQUID PROPELLANT  
EXPOSED TO ELASTOMERIC MATERIALSJOSEPHINE Q. WOJCIECHOWSKI  
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DECEMBER 1989

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<p>The Army is investigating use of LP in large and medium caliber guns. The propellant of primary interest is LGP 1846 consisting of hydroxylammonium nitrate, triethanolammonium nitrate and water. One of the concerns with fielding a liquid propellant system is compatibility with materials used for storage, transfer and handling. The Belvoir Research Development and Engineering Center undertook an investigation on the compatibility of elastomers with LGP 1846. The propellant was collected after exposure to the materials and sent to the Ballistic Research Laboratory for analysis. It was analyzed for a change in fuel and oxidizer content. This report is a compilation of the analysis.</p>					
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We gratefully acknowledge Mr. Ronald A. Sassé for development of the method for correctly determining the level of strong acid impurity.

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## Background

The US Army is currently investigating the use of liquid propellants in medium and large caliber weapon systems. The propellants that have been chosen for the current development program are hydroxylammonium nitrate (HAN) based propellants, LGP 1845 and LGP 1846. These two propellants have the same ingredients; HAN as the oxidizer, triethanolammonium nitrate (TEAN) as the fuel and water as a diluent. The only difference between 1845 and 1846 is 1845 has 3 % more water.

In order to generate a practical system for storage and handling of liquid propellants, it is necessary to know the degree of compatibility with available materials which are likely to be used for transfer and containment of the propellants currently under consideration. The measure of compatibility includes the effect of the propellant on the materials of containment such as swelling of elastomers, corrosion and chemical reactions. The storage compatibility of liquid propellants is also determined by the degradation of the propellant by decomposition, by the solution of ballistically undesirable ions, by solution of materials that result in undesirable changes to the physical properties of the propellant and/or subsequent pressure rise within the storage container.<sup>1-5</sup>

An elastomer and plastic compatibility program was initiated by the US Army Ballistic Research Laboratory (BRL) in 1987. The objective of this program was to measure the compatibility of liquid propellant with various materials of construction by measuring rates of decomposition and reaction under controlled conditions. The approach taken was a three step program. The initial step was exposure of the materials to the propellant. Step two was analysis of materials for degradation or any changes. Steps one and two were performed by the Materials,

Fuels and Lubricants Laboratory at US Army Belvoir Research, Development and Engineering Center.<sup>1</sup> Step three, determination of chemical changes to the propellant itself, was then to be performed at the BRL. This report is a compilation of the propellant analysis.

In developing the list of materials to examine, Ft. Belvoir searched the literature for elastomeric materials compatible with ammonium nitrates. Candidate materials were chosen from the following groups:

- o Butyl Rubbers
- o Chloroprene Rubbers
- o Polysulfonated Elastomers
- o Nitrile Rubbers (including Carboxylated and Highly Saturated)
- o Some Urethanes and Thermoplastic Elastomers
- o Some Fluoroelastomers

Also analyzed were materials from the collapsible tank and hose industries.

In examining the results of the material study, Ft. Belvoir determined that nitrile, nitrile/polyvinylchloride blends, polychloroprenes, fluoroelastomers, halogenated butyl, and ethylene-propylene elastomers performed satisfactorily. Carboxylated nitriles, polyurethanes, and thermoplastic elastomers either totally failed or showed sufficient reduction in properties to label them unacceptable for use with LP.

## Discussion

The materials tested were conditioned in the propellant for several different time periods: 7, 14, 28, 42 and 70 days at 70 +/- 4°F. Samples of propellant were collected at the end of each immersion time. This collection of samples was submitted to the BRL for analysis. The original propellant, LGP 1846 Lot No. ABY86JG2001, was also analyzed prior to exposure to any material for comparative purposes.

The current assay analytical technique for LP 1846 is aqueous titration.<sup>6</sup> Samples were titrated on a Brinkman Instrument Model 672 Titroprocessor and Metrohm 665 Dossimat. Aqueous sodium hydroxide (NaOH) base was used with an approximate 0.25 molarity. Sample sizes were approximately 0.30 grams. Fifty mL of distilled water and 2 mL of acetone were added to each sample. The acetone reacts with HAN to form an oxime and nitric acid and is then titrated with base. Two end points are obtained, one for nitric acid and the other for TEAN. At least two replicates of each sample were analyzed and eight replicates of the control sample were analyzed. The NaOH base was prepared and standardized several times throughout the analysis.

Analysis of several samples showed little change from the control and it was decided that the longest exposure times available for each sample would be analyzed first. If no change relative to the control was evident, intermediate exposure time samples would not be analyzed. This reduced the workload significantly while not affecting the results.

The strong acid impurity was also determined on the control sample. Strong acid impurities could cause decomposition of the LP over extended periods of time. The control had 0.19 wt% excess strong acid, an acceptable level for this investigation.

Sassé developed a new spiked method for measuring excess strong acid in LP that replaces previous BRL methods in use. It was suggested that 1 to 4 mL of 0.25 M  $\text{HNO}_3$  be added to 20 mL of LP diluted with 40 mL of water. Such a small acid addition allows a typical "S" slope titration curve to be developed which is necessary to determine an end point. The sample is titrated with 0.24 M strong base. The method is accurate to below 0.01 weight % excess acid in LP.

### Results

Results of the control analysis are shown in Table 1. Values reported are individual analyses.

Table 1. Titrimetric Analysis of LP 1846 Lot No. ABY86JG2001

	Wt% HAN	Wt% TEAN	HAN/TEAN
	61.0002	20.6333	2.9564
	61.0807	20.2917	3.0101
	61.0429	20.7880	2.9365
	61.1214	20.5543	2.9736
	61.0911	20.3975	2.9950
	61.0206	20.7433	2.9417
	60.9387	20.8026	2.9294
	61.1557	20.6610	2.9600
Average	61.06	20.61	2.96
Standard Deviation	0.07	0.18	0.028

A list of the materials surveyed is provided in Table 2 with appropriate designations. Analytical results for these designations are listed in Table 3. The result reported in Table 3 is the average of two to four actual titrations for each sample. The average and standard deviation of all 100 numbers in Table 3 is given.

### Conclusions

Over 90 % of the values listed in Table 3 are within two standard deviations for both weight % HAN and weight % TEAN. Therefore, there is no statistical basis for claiming chemical reactions of HAN and TEAN. This is not to say that the propellant was not affected as some of the samples showed evidence of change by color and precipitation. Indepth analysis is required on the LP samples of the best material sample candidates.

### Future Work

Examination of the most promising material candidates is planned at temperature extremes. Indepth propellant analysis will be made at that time to include gas products.

**Table 2. Material Designators**

**A. Highly Saturated Nitrile Rubber**

<b>LP-1</b>	<b>NBR-2</b>
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**B. Nitrile Rubber**

<b>LP-2</b>	<b>NBR-8</b>
<b>LP-3</b>	<b>NBR-9</b>
<b>LP-4</b>	<b>1203-F60-R2, RADIANT</b>
<b>LP-5</b>	<b>VT-380 (NBR/PVC), RADIANT</b>
<b>LP-6</b>	<b>BJLT M-40, UNIROYAL</b>
<b>LP-7</b>	<b>0Z0-HA-0221 (70% NBR/30% PVC), UNIROYAL</b>

**C. Carboxylated Nitrile Rubber**

<b>LP-8</b>	<b>XNBR-2</b>
<b>LP-9</b>	<b>XNBR-3</b>
<b>LP-10</b>	<b>XNBR-6</b>

**D. Polychloroprene Rubber**

<b>LP-11</b>	<b>CR-1</b>
<b>LP-12</b>	<b>CR-2</b>

**E. Fluoroelastomers**

<b>LP-13</b>	<b>VITON-1</b>
<b>LP-14</b>	<b>VITON-2</b>
<b>LP-15</b>	<b>REEVES S/4646, (GUM)</b>
<b>LP-16</b>	<b>FLURAN F-5500-A NORTON IND. PLASTICS</b>

**F. Ethylene-Propylene Rubber**

<b>LP-17</b>	<b>REEVES 4601 (GUM)</b>
<b>LP-18</b>	<b>REEVES 4594 (GUM)</b>

Table 2. (cont) Material Designators

**G. Thermoplastic Elastomers**

LP-19	THP-1, ALCRYN R1201 B-70A
LP-20	THP-3, ALCRYN R1101 B70
LP-21	THP-4, MONSANTO GEOLAST
LP-22	THP-5, MOBAY TEXIN 3550R
LP-23	THP-6, MOBAY TEXIN 480 AR
LP-24	THP-7, GAFLEX
LP-25	THP-8, SANTOPRENE, 201-55
LP-26	THP-9, SANTOPRENE, 101-64
LP-27	THP-10, SANTOPRENE, 101-73
LP-28	CD-9250, DISOGRIN
LP-29	NORPRENE, NORTON IND. PLASTICS

**H. Polyurethanes**

LP-30	PU-1, TSE INDUSTRIES, MILLATHANE HT-T10
LP-31	PU-2, TSE INDUSTRIES, MILLATHANE HT-R5
LP-32	TSE-E-34-94, TSE INDUSTRIES, MILLATHANE

**I. Synthetic Rubber**

LP-33	3130 TREAD
LP-34	KRATON 1650, ILC DOVER
LP-35	ATL-644-30, AERO TEC LABORATORIES, INC.
LP-36	GOODYEAR COLLAPSIBLE TANKS GUM

**J. Halogenated Butyl**

LP-37	PE 100A027, ILC DOVER INC.
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**K. Miscellaneous**

LP-38	SANTOPRENE aged 7 days at room temp.
LP-39	REEVES S/4616 aged 7 days at room temp.

Table 3. Titrametric Results of Material Conditioned in Liquid Propellant

Sample	Time, 7 Days		Time, 14 Days		Time, 28 Days		Time, 42 Days		Time, 70 Days	
	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN
LP-1									60.68	20.44
LP-2									61.01	20.45
LP-3							60.53	20.58		
LP-4	59.78	20.10	59.80	19.94	59.96	19.94	59.87	20.10	59.32	20.78
LP-5	59.47	19.98	59.74	20.16	59.84	20.30	59.49	20.23	59.57	20.31
LP-6	58.44	19.42							59.39	20.73
LP-7	59.94	20.02							59.30	20.72
LP-8									62.75	21.13
LP-9									60.89	20.33
LP-10									60.66	20.38

Table 3. (cont) Titrametric Results of Material Conditioned in Liquid Propellant

Sample	Time, 7 Days		Time, 14 Days		Time, 28 Days		Time, 42 Days		Time, 70 Days	
	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN
LP-11									60.69	20.41
LP-12									60.72	20.50
LP-13	60.17	20.06	59.78	19.87	60.04	20.08	60.01	20.05	60.03	20.22
LP-14	60.07	19.95	59.93	20.03	60.07	19.84	60.35	20.34	60.03	20.09
LP-15	59.93	19.76	59.57	20.02	60.08	19.93	60.02	20.16		
LP-16					59.51	19.08	59.44	18.90	58.56	20.60
LP-17	59.64	20.03	59.47	20.13	59.87	20.23	59.43	18.87		
LP-18	59.80	20.12	59.86	20.28	59.93	20.18	59.50	18.81	59.43	18.50
LP-19									59.71	20.09
LP-20			59.89	20.02			59.91	20.05	58.39	20.65

Table 3. (cont) Titrametric Results of Material Conditioned in Liquid Propellant

Sample	Time, 7 Days		Time, 14 Days		Time, 28 Days		Time, 42 Days		Time, 70 Days	
	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN
LP-21							58.66	17.67	60.26	17.95
LP-22	60.62	20.50								
LP-23	61.46	20.51								
LP-24									59.20	19.09
LP-25			59.58	20.02	59.68	20.07	59.90	20.04	58.65	20.58
LP-26			59.92	19.98	59.80	20.09	59.88	20.12	58.63	20.65
LP-27			59.77	20.02	59.51	20.39	60.09	20.05	58.68	20.70
LP-28	62.07	20.44								
LP-29			59.88	19.98	60.03	19.92	59.44	20.78	58.70	20.60
LP-30									60.83	20.69

Table 3. (cont) Titrametric Results of Material Conditioned in Liquid Propellant

Sample	Time, 7 Days		Time, 14 Days		Time, 28 Days		Time, 42 Days		Time, 70 Days	
	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN	% HAN	% TEAN
LP-31									57.03	19.42
LP-32	59.81	19.98	59.45	20.04	59.88	20.35	59.96	20.01		
LP-33	59.92	20.22	59.96	20.04	59.80	20.12	59.94	19.92	58.95	21.24
LP-34	59.68	18.96	59.49	18.80	58.63	20.53				
LP-35	60.59	20.38								
LP-36			59.40	18.52	58.19	20.94	57.82	20.06		
LP-37			59.42	19.03	58.53	20.81	59.62	20.18		
LP-38	60.59	20.53								
LP-39	59.98	20.02	59.97	20.02	60.08	19.93	60.25	20.17		

Global Average: % HAN = 59.77, % TEAN = 20.03

Standard Deviation: % HAN = 0.66, % TEAN = 0.55

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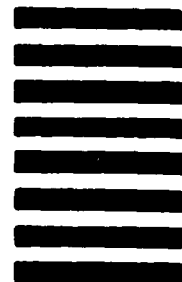
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